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Ultrasoft X-ray Emission Studies

Faculty Supervisor: Alan D. Miller
Assistant Professor, Ceramic Engineering

Graduate Assistant: James H. Rue, Ph.D. Candidate
Predoctoral Research Associate II

Objective: The purpose of the study is to develop an ultra-soft x-ray spectrometer capable of measuring the x-ray spectrum of the carbides and oxycarbides of zirconium in the soft region (10-100Å). Of particular interest are the spectra resulting from transitions involving electrons in bonding states. The information contained in these spectra is of interest in helping to describe the state of chemical bonding in the compounds.

The description of chemical bonding in the carbides of refractory transition metals has been described in a number of ways, however, the interpretation of experimental data is ambiguous at the present time. Part of the problem is a lack of experimental data.

This study seeks to provide additional x-ray spectral data in zirconium carbide and in addition to investigate the effect of dissolved oxygen upon the spectra. One of the unresolved questions surrounding the description of the bonding in these compounds is the sense of transfer of electrons between non-metal p-states and metal d-states. One school interprets the existing x-ray spectra as supporting a transfer from non-meral to metal, while another concludes the reverse. The presence of a strongly electronegative non-metal atom (oxygen) in the carbide lattice should affect the spectra in such a way that an unambiguous conclusion can be drawn.

During the current reporting period, the ultra-soft x-ray spectrometer specimen chamber was completely redesigned and rebuilt to reduce the rate at which the specimen surface contaminates. During the previous report period, satisfactory spectra were obtained, however, they degraded quickly with time with the result that good quantitative data could not be obtained. The new specimen chamber should improve this situation markedly. At present the system is being assembled and checked out. Spectral studies should be under way within two months.

A paper entitled "Current Problems in Interpretation of Ultra-Soft X-ray Spectra" was presented at the 23rd Pacific Coast Regional Meeting of the American Ceramic Society, San Francisco, October 30, 1970.

A paper entitled "Chemical Bonding in Refractory Metal Compounds" was also presented at the above meeting.

Raman Studies of Ceramic Materials

Faculty Supervisor: John W. Macklin
Assistant Professor, Chemistry

Graduate Assistant: Jack C. Surendranath, Ph.D. Candidate
Research Assistant

Objective: The purpose of this project is to measure the Raman spectra of ceramic materials to the end of understanding the character of their bonding.

Information concerning the character and strength of bonding is obtained with difficulty for the highly conducting, opaque transition metal carbides. It is believed that laser Raman spectroscopy will yield definitive revelations concerning bond strengths. The degree of covalency, the effect of carbon content on bond strengths, and possibly the symmetry of the bonds and approximate number of electrons involved in bond formation.

We have obtained tentative laser Raman spectra of powdered and pressed zirconium carbide, and single crystals of vanadium carbide (V_6C_5, 0.84%V; V_8C_7, 0.86%V; and a crystal containing 0.76%V) and titanium carbide (crystal containing 0.93%Ti) using three different laser frequencies (4416, 5145 and 6328 Å) and two scattering arrangements (90° and 180°). Further Raman measurements were made of pressed and powdered zirconium carbide using 4880 and 6471 Å radiation. The Raman spectrum of zirconium oxide (monoclinic) has been measured as a first step in sorting out any features from oxide impurity.

The spectra are generally similar; however, several features, which are identified in both Stokes and Anti-Stokes scans, are variable with exciting frequency and/or temperature. Bands in the region c.a., 250 cm^{-1} are the most persistent. The 180° spectra excited with 6328 Å radiation includes a broad feature which may be low intensity fluoresence. In some scans taken at approximately ambient temperatures, the intensity of the anti-Stokes lines is far greater than that of the Stokes shifts.

For further verification of our Raman measurements and assistance with interpretation, we have measured the infrared absorption spectrum, by conventional and interferometric methods, of thin films (~1 to 3μ thickness) of zirconium and titanium carbide deposited on high density polyethylene by ion sputtering from appropriate samples of the material using a DC voltage. The infrared absorption spectrum shows a broad feature centered between 200 and 450 cm^{-1}. Visible absorption measurements have also been made. Efforts are now being made to verify the composition of these sputtered deposits.

An Argon-Krypton mixed gas laser system from Coherent Radiation Laboratories is now being used as a source for Raman excitation. Apparatus for measuring spectra in a controlled atmosphere and for Raman spectroscopic studies at low temperature has been constructed. Improved gratings for our spectrometer have been ordered. These should reduce spurious spectral features caused by grating defects and improve transmission of the gathered radiation.

Raman measurements at various temperatures will soon be underway. Experiments devoted to understanding the dependence of the scattering measurements upon the incident frequency, including further absorption measurements, are planned. Finally, upon satisfactory interpretation of our measurements, we intend to study the effect of carbon content and other environmental variations upon the Raman spectrum of zirconium carbide.

Zirconium Oxidation

Faculty Supervisor: Thomas F. Archbold
Associate Professor, Metallurgical Engineering

Graduate Assistant: Rangpal Darolia, Ph.D. Candidate
Predoctoral Associate

Objective: This research project has been involved with the determination of the characteristics and mechanisms of the early stages of oxidation of zirconium metal. Thin oxide films have been examined by transmission electron microscopy, and the transformation, twinning, and recrystallization data are being processed. Electron beam heating experiments are providing insight into melting and sintering phenomena. Finally, current work is being done toward the establishment of a detailed investigation of the oxide formed on ZrC single crystals.

In view of the diverse applications of zirconium metal in nuclear, chemical and electronic technology, the oxidation characteristics of the metal have been the subject of numerous investigations over the past two decades. Very few of the results of these investigations were in agreement, and the present research originated as an attempt to resolve the problem. Prior to the work of Dr. L. P. Srivastava on this project, it appeared that few, if any investigators, had taken into account the kinetics of possible surface reactions occuring at the gas/oxide boundary. A preliminary analysis of the available oxidation rate data indicated that the overall confusion could be cleared up when the experimental factors, including surface preparation, were considered. It was decided to reinvestigate the oxidation kinetics and to supplement the findings by the use of transmission electron microscopy of removed oxide films. The attainment of the facilities and the techniques for the study of the zirconium-oxygen reaction during short times would thus be available for a following study of the zirconium carbide oxygen interactions. The overall work would thus assist the general program goal of an intensive study of the zirconium-oxygen-carbon system at elevated temperatures.

I. L. P. Srivastava, Ph.D. research, December, 1968. The oxidation of zirconium was carried out by exposing foil specimens to flowing oxygen, oxygen-air mixtures, air, or oxygen-nitrogen mixtures at temperatures ranging from 440°C to 850°C. The maximum exposure time was 3 minutes, and weight changes were determined after periodic removal of the specimens from the gas stream. The oxidation of both electropolished and abraded specimens follows a combination of a linear rate law corresponding to a surface reaction and a parabolic rate law corresponding to a diffusion mechanism. The oxide formed is a n-type semiconductor below approximately 685°C, and it is a p-type semiconductor above this temperature; the defect concentration in the oxide is oxygen pressure dependent. The diffusion of oxygen occurs via oxygen vacancies in the n-type region and via zirconium vacancies in the p-type region. Relevant thermodynamic parameters for parabolic oxidation have been determined. The linear rate constant for the surface reaction has both positive and negative values. The negative values are attributed to a "passivation" process. A tentative model for an "internal desorption" process has been prepared.

Zirconium Oxidation (continued)

The oxide films formed on electropolished, abraded, and rolled and annealed surfaces of zirconium have been examined by transmission electron microscopy and some correlation between structural and rate information is possible.

M. R. Darolia, M.S. research, December, 1970; Ph.D. research to date. Mr. Darolia expanded Dr. Srivastava's electron microscope techniques, and he carried out a more extensive study of electron beam heating experiments with zirconia films. The foils can be observed to undergo the expected transformations in structure both on heating and cooling. Repeated heating and cooling of the zirconia foil leads to the formation of extremely fine twins; continued heating causes perforations to nucleate and grow. Under appropriate conditions, the zirconia can be locally melted, and an approximate shape analysis of the droplets formed indicates that the surface tension approaches zero with decreasing droplet size. A number of heating sequences have been recorded on videotape. The overall analysis of the needed electron diffraction results has been complicated by some incorrect reciprocal lattice information appearing in the literature, necessitating lengthy recalculations.

In extending the work to study the oxide films formed on ZrC, we have discovered that ZrC single crystals having reasonable dimensions are not available. As a first step in obtaining specimen material, Mr. Darolia has recently produced initial quantities of arc-melted ZrC; attempts to levitation-melt the arc-melted materials will be made as a next step.

Mr. Darolia received his M.S. degree December, 1970. His thesis is entitled "Melting of Zirconia by Electron Beam Heating and Calculation of Surface Tension of Liquid Zirconia."

High Temperature Calorimetry

Faculty Supervisor:	Alan D. Miller Assistant Professor, Ceramic Engineering
Graduate Assistant:	John Negrych, Ph. D. Candidate (NSF Trainee) Predoctoral Research Associate
Objective:	The purpose of this study is to develop a high-temperature isothermal drop calorimeter for use in measuring heat contents of ceramics and related compounds. The current objective is the measurement of heat capacities of zirconium carbide as a function of temperature and carbon content.

The diphenyl ether Bunsen calorimeter developed during this study is a sensitive convenient means of measuring the heat content of specimens from room temperature to approximately 1700°C with the present furnace arrangement. With different furnacing, the temperature capability could be extended to 2500-3000°C.

At the present time the calorimeter is being used to measure the heat capacity of zirconium carbide as a function of carbon content and temperature. Previous measurements of the heat capacity at this laboratory were unsuccessful because of unacceptable contamination of the specimens, with oxygen. The calorimeter atmosphere has since been markedly improved and an oxygen monitor installed in the system. A series of fine specimens ranging in composition from $ZrC_{0.5}$ to $ZrC_{1.0}$ were prepared and analyzed at Los Alamos Scientific Laboratory. The heat content measurements on these specimens will be returned to Los Alamos for post-measurement analysis.

The next task planned using the calorimeter is the measurement of heat capacities in the zirconium oxycarbide phase field. There are indications from vaporization data and from preliminary neutron diffraction studies that at low carbon content and relatively high oxygen content the phase shows ordering in the non-metal sublattice. This ordering reaction may be of sufficient magnitude to affect the heat capacity data.

ZrC Coatings

Faculty Supervisor: Colin J. Sandwith
Assistant Professor, Mechanical Engineering

Graduate Assistant: Leonard Johnson, M.S. Thesis Research
Research Assistant

Objective: The coating-metal interface shear strength and substrate strain that produces permanent deformation in the coating are being evaluated by tensile tests. The long-term objective of these tests is to provide parameters for designing with plasma flame sprayed coatings from an easily reproduced specimen.

The purpose of this project is to develop a test to evaluate the shear strength of flame sprayed zirconium carbide coatings at the interface between the coating and a metal substrate.

Eleven plasma flame sprayed tensile specimens were pulled until the ceramic coatings separated from the substrate. In the first seven tests, using six inch long by one inch wide specimens, the load was increased until either the ceramic coating flaked or the steel substrate fractured. The interfacial shear stress was estimated on the basis of the mean spacing between cracks and the strain at which the ceramic coating flaked off. Depending upon the mean spacing between the cracks, the estimates for different specimens with the same coating varied by an order of magnitude. The variation was attributed first to the nonuniform thickness of the coating and its effect on stress and second to the possibility that the coating did not obey the perfectly elastic model.

Four larger ceramic coated specimens were then tested. A strain gage was mounted on both the coated and uncoated sides of these specimens. Longitudinal strains were measured and in one specimen lateral strains were also measured. One objective was to simultaneously measure the substrate and coating strains. A second test objective was to determine at what substrate strain the coating cracked. Presumably cracks in the coating could be detected by sudden large changes in strain gage readings. A third objective was to measure the residual strain in the coating and substrate after the specimen had been loaded to a certain level.

In order to attain these objectives, the last four specimens were tested as follows. All strain gages were zeroed at zero load. The tensile load was increased in increments of 1,000 pounds to a load of 8,000 pounds; then the load was increased in increments of 250 pounds until the specimen necked down. After each increase, the reading on each strain gage was recorded and the load was decreased to zero, whereupon the reading on each strain gage was again recorded.

Results indicate that the coating elongates permanently even at low loads. This permanent elongation increases linearly with increased strain when the substrate is stressed from 0 to approximately 42,000 psi. Above this stress,

ZrC Coatings (continued)

permanent elongation in the zirconium carbide coating increased very rapidly. No cracks in the zirconium carbide coating were observed until the strain in the coating was greater than 7,000 μ in/in.

The tests showed that the zirconium carbide coating permanently elongated with no observed cracks. Several explanations are possible. The layers of plate-like particles which compose the plasma flame sprayed coating may slide over one another without breaking. Other investigators have shown that there are large residual tensile stresses present in sprayed coatings. Therefore, a relatively small imposed load could cause either the platelets to slide over one another or for some platelets to crack. It is also possible that cracks too small to be seen or measured by the strain gages are occuring, resulting in permanent elongation of the coating. Also the specimens are mounted in parallel chucks. Although precautions were taken to prevent the chucks from bending the specimens, it is not possible to completely eliminate this effect. Tests are in progress to determine the essence of bending caused by the chucks.

Defect Properties of Ionic and Ceramic Crystals

Faculty Supervisors: Thomas G. Stoebe
Associate Professor, Metallurgical Engineering

Richard R. Zupp
Assistant Professor, Metallurgical Engineering

Graduate Assistants: Hira L. Potedar, Ph. D. Candidate
M. Srinivasan, Ph. D. Candidate
Predoctoral Associates

Harshadrai Vora, M.S. Candidate
Research Assistant

Objective: This project concerns the growth and characterization of single crystals of the NaCl structure. Current work indludes studies of mechanical deforamtion parameters in high purity LiF, and crystal growth and mechanical property studies in MgO.

The understanding of the lattice defect structure of NaCl-structure materials is important both in understanding the properties of ceramics with this structure, and in understanding the behavior of other materials systems in general. This study has included material characterization using ionic conductivity studies, and is closely related to other projects investigating optical properties of LiF and MgO.

The current mechanical property studies in LiF and MgO single crystals have included a general characterization of yielding and work hardening as a function of temperature and of purity. Future work will include studies of dynamic strain ageing and the determination of activation energies and volumes at low and high temperatures.

Techniques are needed for growing crystals of controlled composition and defect structure. Continued flux growth experiments are planned, both with A protected Ni crucibles and with Pt crucibles. In addition, a modified arc-fusion method will be used as an alternative means of producing crystals of desired composition. Controlled doping techniqes will be developed for both methods of crystal growth.

The characterization of yielding and work hardening in LiF at and above room temperature is complete. The effects of specimen cross sectional geometry on deformation has been found to be significant in both LiF and MgO. Determinations of activation parameters by stress relaxation in LiF above room temp-rature have been found to be invalid due to dynamic strain ageing.

Additional MgO crystals have been grown in Ni crucibles protected by an A atmosphere. Although some oxidation of the Ni crucible has still been unavoidable, the resulting contamination of the crystals has been minimal, and is mostly present in a thin green surface layer. This surface layer

is readily removed either by grinding or by annealing in vacuum. Although the flux-grown crystals are less pure than those prepared by arc-fusion of ultra-pure MgO, their transmittance in the infrared is not decreased by the impurities present, primarily Ni and Al. The Al is apparently an impurity in the flux constituents. The dislocation density is of the order of $5 \times 10^4/cm^2$, much less than that of crystals grown by arc-fusion. The critical resolved shear stress, as found from indentation wing size measurements, is of the order of 6 kg/mm^2.

Publications

"Effect of Impurities on the Mechanical Behavior of MgO" by M. Srinivasan and T.G. Stoebe. J.A.P. 41, 3726 August 1970.

"Effects of Lattice Defects on Thermoluminescence in Lithium Fluoride Crystals," by T.G. Stoebe, G.M. Guilmet and J.K. Lee, Radiation Effects 4, 189, 1970

"Single-Crystal Growth of Magnesium Oxide by the Flux Method," by H. Vora and R.R. Zupp, Materials Research Bulletin 5, 977-982 (1970)

Accepted for Publication

"Work Hardening Characteristics of LiF Single Crystals," by H.L. Potedar and T.G. Stoebe, Phil. Mag. in press.

Submitted for publication

"Specimen Geometry Effects and Deformation Characteristics in Ionic Crystals" by H.L. Potedar, M. Srinivasan, D.A. Wilson and T.G. Stoebe

Degrees

H. Vora, M.S. Metallurgical Engineering, August, 1970, "Single-Crystal Growth of Magnesium Oxide by the Flux Method."

Mechanical Behavior of Carbon Fibers

Faculty Supervisor: David B. Fischbach
Research Associate Professor
Ceramic Engineering

Graduate Assistant: Roy E. Henrichsen, Ph.D. Candidate
Predoctoral Research Associate I
Union Carbide Grant in Aid

Objective: Investigate the dynamic modulus and internal friction behavior of carbon fibers.

Dynamic modulus and internal friction have proven to be extremely sensitive and valuable techniques applicable to a variety of problems in a wide range of materials. Application of these techniques to conventional, pyrolytic and glassy carbons in the last few years have established that there is considerable structure in the damping spectrum, especially in the temperature range below about 500 °C, and have laid the ground work for interpretation of the dynamic mechanical behavior of carbon materials in terms of structural defects. The dynamic modulus and damping properties of carbon fibers have application significance, and the unusual structure of these carbons suggests the possibility of gaining new fundamental insights into the dynamic mechanical behavior of carbons as well. Particular problems of interest in fibers include the behavior of basal plane dislocations, non-linear elasticity phenomena, and the nature and influence of the fibrillar substructure.

Because of the fibrous form, the torsion pendulum method has been selected as the first line of attack. The very small diameter of the fibers (10 microns or less) causes a number of experimental difficulties. Microminiature techniques are required and mechanical noise and air damping are major problems. For preliminary experiments, a split pendulum with optical readout and electrostatic excitation is being developed. The split configuration (bob attached at the midpoint of a 6 cm fiber hung vertically and fixed at both ends) avoids problems involving the upper suspension required for an inverted pendulum, or the lateral damping arrangement necessary for the standard fixed-free pendulum, and provides electrical contact to both ends of the fiber for direct electrical resistance heating. The optical readout minimized the weight of the bob (a very small mirror on a metal foil holder) and measurement interaction with the pendulum. A laser source and direct-reading photographic paper recording system is being tried. Electrostatic excitation avoids interaction with the earth's field, which is a serious problem encountered when the usual magnetic excitation methods are attempted with these very fine fibers. Initial apparatus design experiments have been encouraging, but a number of problems remain to be worked out. It is planned to investigate the dynamic modulus and internal friction as a function of such parameters as fiber type and structure, torsional strain amplitude, tensile load, and temperature.

Continuum Stress Analysis of Ceramic Materials

Faculty Supervisor: B.J. Hartz
Professor, Civil Engineering

Graduate Assistant: Michael Held (Unsupported) M.S. Candidate
Part-time Graduate Student, Civil Engineering

Objective: To couple the computer oriented numerical "Finite Element Method" of stress analysis with current experimental work in crystalline ceramic materials for a better understanding of materials behavior and porperties and to subsequently invert this process to bring the analytical tools and materials research to bear on the engineering design problem.

During the current semiannual period an attempt was made to shift the emphasis of this phase of the ceramic materials research from using the analytical and numerical capabilities developed mainly to support experimental investigations in ceramic materials science to using these tools for design and interfacing with the design engineer rather than the materials scientist. However, as of the moment, this has not led to any earth-shaking new materials design concepts, but merely to another application, motivated more by design problems, than by research results, but otherwise not much different. This application was to some problems in secondary fracture and crack branching and is briefly described here.

Certain aspects of secondary fracture and of crack branching phenomena were investigated analytically covering a wide range of parameters, such as the location and size of secondary imperfections to cause secondary fracture and the angle of crack branching, and the results are correlated qualitatively with observed cases of secondary fracture and crack branching. The procedures and results appear to have wide application to crack detection and arrest studies, stress corrosion cracking and to studies of fracture in laminated, crystalline, anisotropic and/or non-homogeneous brittle materials, such as concrete and ceramics, for example.

The basic analytical tool involved is a generalization of the Griffith criteria to fracture of non-homogeneous and anisotropic materials with multiple fracture surfaces. This incorporates not only the influence of non-homogeneous and anisotropic materials and of multiple and secondary fractures on the stress distributions and strain energy release rates, but also the differences in surface energies for forming new fracture surfaces such as exist when fracture surfaces follow grain boundaries in crystalline materials or boundaries of inclusions as in the case of concrete and reinforced ceramics.

In order to cover the range of fracture parameters, geometries and anisotropic and non-homogeneous material properties desired the finite element method, utilizing a high speed digital computer, was used as the basic analytic tool to obtain the numerical results for stress distributions and strain energies for the geometries and parameter variations required.

Utilizing the finite element method it was possible to study strain energy release rates associated with incrementing branching cracks at all possible angles of branching and with incrementing secondary fractures assumed to originate at imperfections at various locations relative to a main fracture, as well as with incrementing the main fracture in the presence of any possible secondary fractures. Such a procedure yields immediate indications of the relative probabilities of various branching and secondary fracture possibilities.

In the results to date only symmetrical branching and symmetrical secondary fractures were considered. The results for branching were consistent with many observed cases of branching fractures and offer an alternative explanation of the branching phenomena. The results for secondary fracture depend upon the presence of secondary imperfections and although no observations directly applicable to the symmetric cases studied were found, the results are seen to be qualitatively in agreement with available test results and observed performance fractures.

Current studies are aimed at application of this procedure to stress corrosion fracture of laminated materials. For these applications, additional fundamental material property information on free surface formation in corrosive environments and on initial interfacial lamina boundary and free surface energies is needed. A final current application is the possibility of predicting and improving crack arrest characteristics of sheets with striations or unidirectional imperfections or "reinforcers," since with this procedure it is possible to determine the size and angle of cracks which will propagate through the transverse striations and which will branch or be arrested by the striations or "reinforcements."

During the period covered by this semiannual report this work digressed into some application into secondary cracking and crack branching. This is being written up for submission as a technical paper.

Thermal Stresses in Crystal and Ceramics

Faculty Supervisor: Max D. Coon
Assistant Professor, Civil Engineering

Graduate Assistant: Maurice B. Cooper, Ph. D. Candidate
Predoctoral Research Associate
(terminated September 1970)

Objective: The objective of this study is to make use of the ductility of ceramics at high temperatures to introduce residual stresses in such a way as to improve the load carrying capacity of structural elements.

This is a theoretical and experimental study of residual stresses in ceramic materials. A favorable residual stress pattern may improve some ceramics as load carrying materials as evidenced by some pre-stressed glasses. It is well-known that rapid cooling of some ceramics may introduce residual stresses. Another procedure which seems worth investigating involves making use of the ductility of ceramics at high temperatures. The thought here is to heat the material until it is ductile and then load it followed by a subsequent cooling and unloading. It is felt that this procedure may induce favorable residual stress patterns on certain instances.

For the series of experiments being conducted, the structural component will be a rectangular beam subjected to three point loading. The amount of favorable residual stress will be measured by comparing the failure strength of untreated beams with that of treated beams. The actual heat-load cycle needed to induce these stresses will be studied. For example, heating to a temperature where a considerable amount of plastic deformation is available and then loading-unloading and cooling may leave a stress pattern similar to that which would occur in mild steel at room temperature. On the other hand, the frozen stress technique of photoelasticity is one where the component is loaded-cooled and unloaded. In the series of tests, several programs of loading and heating will be tried in an attempt to prove this basic hypothesis.

It seems worthwhile to describe the ideal material for these tests. First, at room temperature the behavior should be elastic-brittle (i.e., no plastic or viscoelastic response). Second, at some elevated temperature the behavior should change to elastic, ideally plastic, with a reasonable amount of ductility and higher yield stress in compression than tension. Preliminary calculations indicate that this difference in yield stresses may induce compressive residual stresses in both the top and bottom of the beam.

To find a real material that comes as close as possible to the ideal, one needs a considerable amount of test data in tension and compression over a wide temperature range to establish the transition from brittle to ductile behavior. It is also helpful to have some available test data in bending. Obviously the more data available, the less preliminary testing will be required.

On reviewing available experimental data, titanium carbide was chosen as the test material. The titanium carbide has been obtained and the beam specimens prepared. A series of room temperature tests, in three point loading, have been conducted. The carrying capacity of heat treated beams will be compared with these results. A furnace element and container have been constructed and assembled.

Nondestructive Determination of Residual Stresses

Faculty Supervisor: Robert J. Campbell
Assistant Professor, Ceramic Engineering

Graduate Assistant: Derrille Thayer, M.S. Candidate
Research Fellow (Orton Ceramic Foundation Fellow)

Objective: This research is aimed at proving the feasability of determining porosity in bodies by non-destructive techniques. The use of ultrasonic pulse transmission related to elastic modulus at ambient and high pressures is being pursued.

This research attempts to measure stresses in fired bodies by non-destructive tests. These determinations will permit estimation of the effect of such stresses on properties such as thermal shock and ultimate strength.

The measurements of stresses have been oriented toward detection by ultrasonic tests. It was postulated that sonic velocities within a sample would be sensitive to changes of stress within the sample. It was expected that such a non-destructive test would permit production line testing of products. Detection and removal of stressed parts could prevent eventual failure of devices.

Samples of a whiteware type body were fabricated with varying amounts of glass content created by differences in soak times on firing.

A reflectoscope proved to be inadequate to detect sonic pulses through the samples. A different approach was used by employing an ultrasonic pulse detection while the sample was pressurized. This system provided better coupling between transducers and sample. Ware velocities were determined by super positioning the trace of the signal through the sample and a trace of a signal through a mercury delay line. The length of the mercury delay line provided a calibration of transit time.

First indications are that this may be a rapid method of determination of porosity rather than strain in the ceramic pieces. More samples with greater ranges of porosity are being prepared for confirmation.

Strain Energy in Crack Propagation

Faculty Supervisor: Robert J. Campbell
Assistant Professor, Ceramic Engineering

Graduate Assistant: Sang Moo Park, M.S. Candidate
Research Assistant

Objective: An attempt is being made to correlate energy involved in propagation of cracks through polycrystalline bodies. $BaTiO_3$ bodies were chosen for models because previous work had suggested limited plastic behavior.

This project was originally intended to examine the strain energy requirements for propagation of a crack in single crystals. The intent was to employ a single crystal of $BaTiO_3$ with two areas of polarization established to provide a calibrated strain input. The amount of strain could be related to the electrical field applied.

The project was stimulated by knowledge of failure of polycrystalline underwater transducers as a result of high power service. It is anticipated that this research may permit improved design of such equipment.

Difficulties in obtaining adequate crystals have shifted the current work to a study of energies in breaking polycrystalline $BaTiO_3$. Some earlier work attempting to measure Young's modulus in $BaTiO_3$ had indicated non-elastic behavior at low stresses. Some permanent deformation was observed in samples at stresses which did not cause fracture.

It was postulated that some part of the mechanism might be grain boundary sliding or something connected with domain shifting. To investigate this possibility a number of small $BaTiO_3$ prisms have been produced with notch stress concentrators. The samples are strained to failure in a 4-point loading fixture on an Instron testing machine. Any abrupt changes of crystal boundaries or other rapid absorption of energy in the crystal lattice are expected to produce accoustic vibrations. These vibrations are detected by a phonograph pick-up and recorded on magnetic tape. The correlation of the accoustic recordings with the load cell records are proceeding.

Photographic studies have been made in an attempt to determine the mode of fracture in polycrystalline $BaTiO_3$. The fine grain structure of the samples has made it difficult to determine whether the crack propagates in an inter-granular or trans-granular fashion.

Interfacial Energy of Low Angle Tilt Boundaries

Faculty Supervisor: William D. Scott
Associate Professor, Ceramic Engineering

Graduate Assistant: G. Achutaramayya, Ph. D. Candidate
Predoctoral Research Associate II

Objective: The purpose of this project is to determine the relative interfacial energy of low angle dislocation wall tilt boundaries formed by polygenization of deformed aluminum oxide crystals.

This research is an attempt to test theories of simple grain boundary structures by measuring the variation of boundary energy with misorientation. Simple low angle dislocation tilt boundaries have been developed in alumina single crystals by controlled deformation on basal planes followed by a high temperature polygenizing anneal.

During the period covered by this report an extensive computer program has been developed to utilize a digitizer to produce an analytical expression for the thermally grooved surface topology. This was done by converting interferometer fringes into x-y coordinate parts and manipulating the resulting data. The results of this work indicate that the reproducibility and accuracy of curve measurements by this technique is as good, but no better, than manual techniques.

Although the present work is primarily concerned with relative interfacial energies as measured from equilibrium thermal grooves, additional information can be obtained from the kinetics of polygenization and groove formation. Polygonization kinetics yield information on dislocation climb and bulk diffusion while the groove growth kinetics give information on surface diffusion. The following experiment is now in progress. A thin, plate-like single crystal was deformed in bending into a u-shape to introduce dislocations. It was then sliced into six thin u-shaped specimens each about 0.5 mm. thick. These identical specimens will then be annealed at various times and temperatures to obtain the required measurements. The following information will be obtained: Rate of polygenization and groove growth as a function of time and temperature, and the final equilibrium groove angle which is related to the interfacial boundary energy.

Mobility of Grain Boundaries in Alumina

Faculty Supervisor: William D. Scott
Associate Professor, Ceramic Engineering

Graduate Assistant: Robert H. Burns, Ph. D. Candidate
Predoctoral Associate II

Objective: To measure the mobility of well-characterized low angle grain boundaries under the influence of surface energy and electric field driving forces.

Grain growth involves boundary migration and this project is attempting to obtain quantitative information on rates of movement of well-characterized boundaries. The response of a boundary to an electric field will also give information on grain boundary structures.

Three types of specimens will be used in this work. The first is a rectangular specimen with a grain boundary through the center dividing it into two cubes. An electric field will be applied across the ends normal to the boundary and movement of the boundary will be measured relative to two hardners indentation markers. This type of movement has been observed in the present works.

The second configuration is a triangular specimen with a boundary parallel to the base. Boundary migration should be towards the apex of the triangle under the driving force of reduced boundary area. Migration will be measured at intervals over various times and temperatures.

The third configuration consists of a rectangular specimen with a boundary parallel, and very close to the rectangular face. In this case, movement of the boundary is started by curving the boundary up to the surface at one end and allowing it to sweep the length of the crystal.

The information on kinetics of grain boundary motion will be useful in understanding grain growth and sintering of alumina.

Relative Energy of Deformation Twin Boundaries in Alumina

Faculty Supervisor: William D. Scott
Associate Professor, Ceramic Engineering

Graduate Assistant: Om P. Bhandari, M.S. Candidate
Research Assistant

Objective: To evaluate technique of thermal grooving as a method of measuring interfacial energy and to measure twin boundary energy in alumina.

Deformation twins provide a convenient way to produce straight, clean boundaries in alumina. The relative energy of these twins is quite high and good thermally etched boundaries can be produced.

The relative energy of twin boundaries has been measured relative to $(11\bar{2}0)$ and $(1\bar{1}00)$ planes and relative to several random planes at various angles of twin-surface intersection. Over 140 such measurements have been made on 25 twin boundaries, and all conditions gave a relative energy (twin energy/surface energy) of 0.312 (std. dev. 0.034).

This result indicates that the variation of free surface energy in alumina is low. Furthermore, annealing conditions for thermal groove formation were in tungsten and in pure sapphire crucibles and no difference in relative energy was observed.

In one case the annealing system became contaminated with ZrO_2, and relative energy values changed to 0.47 which indicates a reduction of surface energy by the contaminant of 34%.

The results of this investigation show that the twin interfacial energy in alumina is higher that that of metals by a factor of ten or more and that the surface energy of alumina does not vary greatly with orientation.

Surface Diffusion Studies

Faculty Supervisor: Alan D. Miller
Assistant Professor, Ceramic Engineering

Graduate Assistant: Edward H. Randklev, Ph.D. Candidate
Predoctoral Associate II

Objective: This study is concerned with the investigation of surface diffusion and the phenomenon of linear thermal faceting of surfaces of single crystal aluminum oxide. The thermal faceting behavior of the system relative to the growth and morphology versus temperature, time, and atmosphere condition is expected to provide information regarding the anisotropy of surface energy of the system and the relative transport rates on the surfaces involved.

The behavior and specific properties of the surfaces of oxide has until recently received only minor attention in the research of materials. The present study was chosen to attempt to provide such information relative to elevated temperature ($\geq 1500^{\circ}C$) for an important and well characterized oxide such as (single crystal) aluminum oxide (Al_2O_3). In an effort to maintain the high quality of the starting material and preserve its hopefully intrinsic behavior at such elevated temperatures, considerable time was devoted to providing heat treating facilities and, especially, fixturing and containers, which interfered as little as possible with the surfaces being studied. For instance, a crucible and cover for the heat treatment container were constructed from the same material as the specimens themselves. The morphology and growth of the linear thermal facets and other surface features developed are being studied via optical microscopy, scanning electron microscope, x-ray diffraction, and electron microprobe in the case of doped systems. The kinetics data to be used in the determination of property behavior is being obtained via optical interference microscopy. The use of a soon to be installed scanning scope in the department will allow completion of this part of the analysis already begun elsewhere.

All literature review and equipment construction have been completed and the total project is near completion. It was initially proposed that the surface diffusion of an impurity element (chromium - the only component found to be predictably successful to work with) on specific surfaces of aluminum oxide would be studied. This work was completed, after careful preparation, through the initial diffusion anneals and analysis and was terminated when it was determined that vapor transport dominated the movement of the chromium at the temperatures necessary for the study. It is to be noted that particular care was given to provide a high purity argon atmosphere for these anneals so as to avoid the common oxidation mode of vaporization of chromia (Cr_2O_3) found in environments containing appreciable oxygen. The point source model for investigating surface diffusion was found to be physically applicable to an oxide system, contrary to certain general remarks in the literature.

The thermal faceting investigation of the aluminum oxide system has progressed down to the final stage of observing the growth kinetics of individual linear facets. The system has been surveyed as to its occurrence with respect to surface orientation (basal, rhombohedral or prismatic), crystallographic direction, atmosphere (oxidizing, reducing, "neutral") and temperature (1500°C-1900°C). Work regarding the driving force for formation of the linear facets under conditions with and without closed crucible (sapphire) and on mechanical, and on chemical polished surfaces indicates that it is surface energy driven. Additional features such as thermal and chemical dislocation etch pits have also been looked at in order to identify features found on annealed surfaces.

U-V Photolysis-Radiation Ceramic Studies

Faculty Supervisor: James I. Mueller
Professor, Ceramic Engineering

Graduate Assistant: Coimbatore S. Krishnan, Ph. D. Candidate
Predoctoral Associate I

Objective: To understand the luminescence mechanism of impurity ions in ultra violet irradiate MgO single crystals using thermoluminescence and electron spin resonance techniques with a view to stabilize MgO from U-V degradation by controlled doping with compensating ions.

It is well known that many ceramic pigments are severely discolored and change their optical and thermal absorption properties when exposed to intense U-V irradiation, such as from the sun. In pigments used as spacecraft thermal control coatings the problem is critical since U-V degradation may drastically alter the solar absorbance of white coatings; endangering the thermal stability of the vehicle. TiO_2, Sb_2O_3, ZnS and ZnO are the pigments currently used, ZnO having been found the most stable in laboratory U-V environments. MgO, which has long been used as a standard for reflectance measurements, is a possible candidate for such coatings if stabilized against U-V degradation since it is a ceramic compound of exceptional properties (high melting point, isotropic optical properties etc). Besides it is an excellent inert matrix in which the luminescence and optical absorption characteristics of transition metal ions may be studied. Ionizing radiation, such as U-V, X-rays and γ -rays, merely ionize the impurity ions present and do not in themselves cause F centers by atomic displacements. Hence over long periods in severe space environments, U-V stabilized MgO might perform better than the other coatings. Neutron irradiation causes slow changes in optical absorption by production of F centers and this property may be exploited in thermal control coatings of nuclear powered deep space vehicles where an increasing absorptivity with time is required.

While much work has been done to understand the optical and magnetic properties of impurity and color centers in MgO and other alkaline earth oxides, many puzzling aspects, such as the blue luminescence of some undoped MgO single crystals, still remain. If the fundamental defect mechanisms by which U-V energy is absorbed and released are clearly understood, it might be possible to stabilize MgO against U-V degradation of optical properties by addition of stabilizing ions. The goal of the present study is to investigate the luminescence of Mn ions in U-V irradiated MgO single crystals and the possible effect of additional ions as stabilizers using thermoluminescence, thermally stimulated conductivity, optical absorption and electron spin resonance.

The following accomplishments have been made:

1) An extensive literature review of ESR spectra of transition metal ions in MgO was made.

2) Thermoluminescence intensity of MgO single crystals was found to decay at a rather slow rate after U-V irradiation, thus making it feasible to transfer samples after irradiation to the ESR spectrometer.

3) The sample holder of a locally constructed ESR spactrometer was modified to hold crystal samples.

4) Several preliminary ESR spectra of an MgO crystal were obtained to establish feasability of the spectrometer for the present study.

5) Mn^{2+} ion has been tentatively identified in octahedral symmetry as the dominant paramagnetic species in the sample studies.

6) Several designs were made to construct a suitable high temperature furnace for vacuum annealing and doping of single crystals.

Irradiation Damage of Sapphire & Ruby

Faculty Supervisor: James I. Mueller
Professor, Ceramic Engineering

Graduate Assistant: John M. Rusin, Ph. D. Candidate
Predoctoral Research Associate I

Objective: The purpose of this research is to study the pre-existing defects in sapphire and the effect of U-V colors on optical degradation in ruby lasers.

It appears that there is great need for a basic study on inherent defects in pure sapphire. These defects are considered to be either lattice imperfections of the host crystal or impurity ions. A study on pre-existing defects in sapphire and their effect of U-V coloration should partially solve the problem of orange degradation in ruby lasers.

Many studies have been conducted on radiation damage of sapphire and ruby. The effect of radiation has been mainly studied by optical absorption, electron spin resonance, and thermoluminescence. The more recent investigations have been to study the causes responsible for degradation of performance of ruby lasers.

Ruby and sapphire, as received from the manufacturer, have been found to contain absorption color centers of varying amounts. Levy has shown that the three color centers in synthetic sapphire can be removed by heating at 1300°C for 3 hours. No high temperature annealing effect has been studied on ruby.

Gamma and reactor irradiation produce color centers in both ruby and sapphire. Heating of irradiated crystals produce thermoluminescence and bleaching of color centers if annealed around 700°C.

Thermoluminescence has been studied for both gamma and reactor irradiated sapphire and ruby single crystals. Very little study has been made of purely U-V irradiation induced thermoluminescence. Radiation from xenon flash lamps (200 to 400 nm) has been found to produce "orange" degradation of laser ruby. The output energy of the ruby laser can be partially restored by heating to 900°C for 24 hours.

The manufacturerers of sapphire and ruby use two basic methods: pulled from a melt using the Czochralski method or by the Verneuil process in which powder fed through a flame is impinged on the surface of a liquid puddle on the growing crystal.

Thus it is planned to first study the effect of annealing in various atmospheres on optical density, irradiation damage, and TL. This should be first conducted on various samples from the same boule and then comparison can be made between boules from different manufacturers and manufacturing techniques. Once the effect of heat treatment is established, then the effect of impurities can be studied.

Domain Dynamics in Isomorphous Ferroelectrics

Faculty Supervisor: John L. Bjorkstam
Professor, Electrical Engineering

Graduate Assistants: Guy J. Adriaenssens, Ph.D. Candidate
Predoctoral Research Associate II

James I. Aikins, M.S. Candidate
Unsupported

Objective: To relate cooperative atomic effects near the phase transition in KH_2PO_4(KDP) type ferroelectrics to macroscopic dielectric phenomena; particularly domain formation and propagation.

Work on this project was initiated primarily in order to understand the relationship between cooperative hydrogen motion in KDP type ferroelectrics and macroscopic dielectric phenomena which accompany the phase transition. In addition to the technological importance of this class of crystals because of their effectiveness as optical modulators, they provide an exceptional system in which to study the nature of the hydrogen-bond.

Prior to our studies it was known that dueteration shifted the phase transition temperature T_c $\simeq$ upward by $\simeq$ 100°C. While deuteration has similar effects on virtually all hydrogen-bonded ferroelectrics, in KDP they are the most striking. Our initial observations of several orders of magnitude difference in domain mobility between KH_2PO_4(KDP) and KD_2PO_4(KDP) emphasize this difference probably as much as any observed phenomenon[1,2].

Because of the particular relationship between orientation of the optical index in antiparallel domains, light trapping occurs in alternate domains, and crossed-polarizers are unnecessary for domain observation. As a result these crystals are particularly suitable for studies of optical properties of 180° domain formation and propagation[3]. Domains are unaffected by the presence of poling electrodes[4].

We have previously reported the observation of low frequency ($\leq$100 HZ) dielectric relaxation near T_c ($T-T_c \lesssim 3.5$°C) in KH_2AsO_4[5]. This relaxation phenomenon occurs at a much lower frequency than observed for any other ferroelectric, and seems to be related to a long range correlated hydrogen motion predicted by Matsubara and coworkers,[6]

for a two-dimensional model system similar to KDP. Our most recent efforts have been directed toward a precise evaluation of the relaxation time and activation energy, just above and below T_c. Reduction of the initial data indicates a single relaxation time. This seems a particularly fortuitous result, and is being carefully checked.

Results of the dielectric relaxation experiments will be compared with apparently related phenomena observed in the As^{75} nuclear magnetic resonance (NMR) spectrum of KH_2AsO_4.[7,8] The NMR experiments have previously been supported by the National Science Foundation. Both the dielectric relaxation and NMR experiments are currently being carried out by Guy Adriaenssens and will be included as part of his Ph. D. thesis. The initial dielectric relaxation results will soon be submitted by James Aikins in partial fulfillment of the M.S. requirements.

Publications

1 J.L. Bjorkstam and R.E. Oettel, The Trend (University of Washington) 17, 8 (October 1965)

2 J.L. Bjorkstam and R.E. Oettel, Proceedings of the International Meeting on Ferroelectricity, Prague, Czechoslovakia, 1966. Edited by V. Dvorak, A. Foreskova, and P. Glogar. Vol. II, pp. 91-96.

3 R.E. Oettel, M.S. thesis, University of Washington (December 1965).

4 J.L. Bjorkstam and R.E. Oettel, Phys. Rev. 159, 427 (July 1967)

5 Progress report of June 15, 1970

6 N. Ogita, A. Veda, T. Matsubara, H. Matsuda, and F. Yonezawa, J. Phys. Soc. Japan 26, Supplement, 145 (1969).

7 R. Blinc and J.L. Bjorkstam, Phys. Rev. Letters 23, 788 (October 1969).

8 J.L. Bjorkstam, J. Phys. Soc. Japan 28, Supplement, 101 (1970).

Studies on GASH

Faculty Supervisor: E.C. Lingafelter
Professor, Chemistry

Graduate Assistant: Louis F. Torre (Ph. D. Candidate), Res. Assist.

Objective: To use x-ray crystallography to determine the structural changes which occur when the ferroelectric material Guanidinium Chromium Sulfate Hexahydrate is subjected to an electric field, and to infer the mechanism for the rearrangement. Hysteresis loops of the crystal will be monitored to indicate changes in the dielectric properties.

Techniques were developed for obtaining single crystals of the ferroelectric material Guanidinium Chromium Sulfate Hexahydrate (GCrSH) which were suitable for study by x-ray diffraction (about .3mm on the side of a cube). A method was devised for applying a graphite colloidal dispersion to form electrodes on two opposite faces of the crystal. Copper wires (about .001 inch diameter) were attached to the electrodes and connected to external circuitry used to pole the crystal with both ac and dc electric fields. Equipment was assembled to monitor both the 60 cycle ac and variable frequency quasi-static hysteresis loops. The hysteresis loops were used to determine an appropriate dc field to apply to the crystal to maintain it in a state of saturation polarization, and also to detect changes in the ferroelectric properties upon exposure to x-rays and electric fields. It was found necessary to enclose crystals in a dielectric material to prevent arcing when the crystals were exposed to x-rays while being poled with an electric field.

Several attempts were made to collect x-ray data from crystals which were poled in different ways to states of polarization. Because the crystals seemed to deteriorate, a systematic study of selected reflections was carried out on a manual diffractometer to determine their behavior when the crystal was subject to varying conditions. While some results are still not yet understood, in general it was found that while the crystal was maintained in one of its saturated states, it did not decompose upon exposure to x-rays. When the crystal was alternately brought to each of its two possible states of saturation polarization and exposed to x-rays then the observed reflections decreased in magnitude. No amount of direct and alternate current poling at different magnitudes of the applied voltage could restore the originally observed magnitudes. Eventually the crystal decomposed.

A full set of data was collected on the automatic x-ray diffractometer while the crystal was maintained in one of its states of saturation polarization. However, when the polarization was reversed the crystal eventually deteriorated. Analysis of the first complete set of data indicated that the crystal was definitely poled to one of its saturated states and the absolute sense of this structure could be determined. However, the index used assessing the suitability of the model to the data was less satisfactory than expected. This may be due to the difficulty of applying a satisfactory correction for absorption when the absorption coefficient is high. However, it is suspected that the crystal may yet have a small amount (c. 10%) of domains poled in the opposite sense and this would represent a disorder in the crystal which could prevent a satisfactory solution of its structure. This hypothesis is currently being studied.

Ceramic Processing - Compaction

Faculty Supervisor: O. J. Whittemore, Jr.
Professor, Ceramic Engineering

Graduate Assistants: Daniel B. Leiser, Ph.D. Candidate
Predoctoral Associate II

Arun K. Chattopadhyay, M.S. Candidate
Research Assistant

Objective: To study compaction of ceramic particles. Statistical analyses are being made of the interrelationships of variables in compaction including material, particle size, particle shape and compaction rate.

Compaction, or pressing, is the forming method used for the largest value of ceramics. To provide a better understanding of this process, these variables were studied - particle size, particle shape, material, loading rate, and pressure. Three fused ceramic materials were used - mullite, magnesia and alumina. The mullite was used in two particle shapes, equi-axed and angular.

Compaction was studied by compressing single sizes at several constant rates and measuring pressure vs. compaction. After compaction, particle breakdown was measured by sieving. Compaction curves were first analyzed by attempting to fit various empirical equations. It was concluded that compaction behavior of ceramic materials cannot be described by a single empirical equation basic to the process.

Statistical analyses of variance were then determined on the several variables and on the interaction of variables. These interactions were found very significant: loading rate vs. pressure, loading rate vs. material, loading rate vs. particle shape, and particle size vs. material. Fused magnesia was demonstrated to have different compaction behavior (more like metals) than other ceramic materials, and this is associated with the ductility others have found in this material.

Mr. D. B. Leiser has nearly completed his dissertation encompassing the information described above and plans to complete his degree in January, 1971. Mr. Chattopadhyay is preparing his plan of study of compaction of binary mixtures of sizes of fused alumina.

A paper entitled "Compaction Behavior of Ceramic Particles" by D. B. Leiser and O. J. Whittemore, Jr., was published in the Amer. Cer. Soc. Bulletin, 49, 8, 714-7 (1970).

A paper entitled "Ceramic Powder Compaction Studies Using a Glass Sphere Model" by D. J. Calkins and O. J. Whittemore, Jr., has been submitted for presentation at the annual meeting of the American Ceramic Society, May, 1971.

Ceramic Processing - Sintering

Faculty Supervisor: O. J. Whittemore, Jr.
Professor, Ceramic Engineering

Graduate Assistant: J. Joseph Sipe, Ph.D. Candidate
Predoctoral Research Associate

Objective: To study the initial stage of sintering where pore growth occurs. Pore growth has been shown to occur during the initial sintering of Fe_2O_3 and MgO, and under certain conditions, Al_2O_3.

Sintering is the thermal process used for manufacture of most ceramics. It determines the final microstructure and is responsible for many of the final properties. When most ceramics are sintered, shrinkage occurs. However, when certain fine grained ceramics are sintered, a stage of pore growth has been shown to occur prior to shrinkage. This stage has been shown to occur in Fe_2O_3 and MgO, in Al_2O_3 under some conditions, but not in ZrO_2.

Studies were conducted by preparing compacts of the oxides at various pressures and sintering the compacts in air at varying temperature and time. Pores were measured by mercury intrusion, and conclusions reached from these data were confirmed by electron microscopy and by scanning electron microscopy (SEM).

The oxide, Fe_2O_3, was selected for most of the work, since the mechanism for the initial sintering of this oxide is generally agreed on (e.g., grain boundary diffusion) and because well-characterized, fine spherical particles were available.

A pore growth model, the "fast pairs" hypothesis, has been proposed, where some fraction of particle pairs sinter at a much greater rate than the bulk. Thus within the mass, "fast pairs" can merge causing pore growth yet no shrinkage. Utilizing this hypothesis, mathematical relationships were derived for both grain boundary diffusion and volume diffusion as the modes of material transport. The relationship

$$r^{4/3} - r_o^{4/3} = 2\lambda \left[\frac{3\gamma\Omega b D_b}{2kT}\right] 1/3 \quad t^{1/3}$$

was obtained for grain boundary diffusion, where

r_o = initial pore radius

r = instantaneous pore radius

λ = fraction of "fast pairs"

γ = surface energy

Ω = atomic volume

b = grain boundary thickness

D_b = grain boundary diffusion coefficient

k = Boltzmann's constant

T = absolute temperature

t = sintering time

Kinetics of pore growth in Fe_2O_3 conformed to this model and the calculated diffusion coefficients agreed with reported values derived from densification kinetics. Average particle size (measured by SEM) increased at approximately the same rate as the pore size, in agreement with the model. The existence of fast pairs was confirmed by measuring rates of neck growth by electron microscopy.

Mr. J. J. Sipe completed the requirements for the Ph.D. degree in November, 1970. His dissertation is entitled "Pore Growth During The Initial Stages of Sintering." A paper based on the dissertation has been submitted for presentation at the annual meeting of the American Ceramic Society, May, 1971. A note entitled "Preparation of Samples for Sintering of Submicron Particles by Transmission Electron Microscopy" by J. J. Sipe and O. J. Whittemore, Jr., was published in the Jour. Amer. Cer. Soc. 53, 9, 525 (1970).

This work will be contined by Mr. K. Aihara who will enter the University in January, 1971. His work will concentrate on studies of pore growth during the initial stages of sintering MgO.

The Graphitization Process

Faculty Supervisor: David B. Fischbach
Research Associate Professor
Ceramic Engineering

Objective: The influence of various microstructural and processing parameters (initial microstructure, internal stress, hot deformation, etc.) on the development of crystalline order in initially disordered carbons is being investigated to gain a better understanding of the graphitization process.

Crystalline hexagonal graphite is generally agreed to be the thermodynamically stable form of solid carbon under all conditions except very high pressures. However, carbons commonly occur in other metastable crystalline (e.g., diamond) and disordered (e.g., cokes, carbon blacks, pyrolytic carbons, glassy carbons, etc.) forms which tend to transform to graphite under conditions (such as very high temperatures) providing sufficient molecular mobility. This complex graphitization transformation, which results in significant changes in properties, is one of the most fundamental processes in the science and technology of carbon materials, but it is not yet well understood. The graphitization behavior of disordered carbons varies greatly, depending on the precursor material and the carbonization conditions used in the preparation. "Non-graphitizing" carbons (e.g., glass-like carbons, carbon fibers) are very resistant to graphitization by thermo-mechanical treatment and retain very disordered structures even after annealing or hot-working in the range 2700-3200°C. This structural stability appears to be related to poor development of the graphitic layer-plane structure during carbonization, and the extreme difficulty of obtaining any true recrystallization in solid carbons. "Graphitizing" carbons (e.g., conventional petroleum and pitch cokes, high deposition temperature pyrolytic carbons, etc.) transform more or less completely to graphite on annealing in the range 2500-3000°C. The process is thermally activated with a single effective activation energy, and is generally enhanced by hot-working. Even in this class of carbons, there is a wide range of graphitization behavior depending on the origin and type of carbon. This evidently derives from differences in the detailed microstructure, internal stresses, etc. Much remains to be learned about the nature of the defects which produce and stabilize the disordered structure, and the mechanisms by which these defects are removed by annealing or hot-working. The present research effort is addressed to this general problem area.

Shear deformation parallel to the basal planes would be expected to play a dominant role in the effect of hot-working on graphitization. Basal shear is the easiest mode of deformation in graphitic carbons; and layer curvature, interlayer defects and layer stacking disorder are important structural characteristics of disordered carbons. Using x-ray diffraction techniques the structures of adjacent deformed and undeformed regions of pyrolytic carbon specimens which had been sheared parallel to the average basal plane orientation at 2500-3000°C are being determined and compared. In the samples analyzed to date both the deformed and the undeformed regions have been well graphitized and little influence of shear has been detected. In order to realize significant shear strains prior to fracture, it was necessary to anneal

the specimens at high temperatures prior to deformation. This anneal evidently caused substantial graphitization. The shear deformation was carried out as part of an earlier research program at the Jet Propulsion Laboratory. The equipment used is no longer available. The stock of deformed specimens in hand is therefore being surveyed in an attempt to identify those with minimum annealing treatment in which the degree of graphitization may be sufficiently low to detect any influence of deformation.

To obtain information on the influence of internal stresses on graphitization, the graphitization kinetic behavior of powder samples has been compared with that of solid samples for several high deposition temperature pyrolytic carbons. Powder (smaller than 200 mesh) and solid (1.1.5 and 3.3.3 mm^3) samples of the same carbon were isothermally annealed at the same time at temperatures in the range 2400-3000 ^{o}C for cumulative times ranging from a few minutes to about 20 hours. Powder samples were also prepared from the solid cube samples after completion of the annealing series. The progress of the graphitization transformation was followed at room temperature by x-ray diffraction analysis (powder and stick samples) and diamagnetic susceptibility measurements (cube samples). Sample form had no effect on either graphitization rate or activation energy within experimental error. It is concluded that "long-range" ($\geq$50 μm) internal stresses, which should be affected by powdering, do not play a very significant role in the graphitization of pyrolytic carbons. Comparison of the graphitization behavior of a number of pyrolytic and conventional carbons indicates that short-range stresses and/or microstructure do not appear to have a significant effect on the activation energy either, but they do influence the rate and shape of the graphitization vs. time curves of graphitizable carbons, evidently through the effective pre-exponential factor.

An extensive review of the literature on the kinetics and mechanism of graphitization, the carbonization process and the structure of disordered carbons has led to the development of a simple "working hypothesis" model for the graphitization process. In brief, it is suggested that graphitizable carbons can be considered as defective graphites. Graphitization occurs by improving the existing disordered structure by annealing out the defects which produce or stablize the disorder. The fundamental thermally activated rate-determining process is self-diffusion by defect mechanisms. Differences in behavior among various carbons result from differences in pre-exponential factor distributions which are related to the detailed microstructure (layer plane size and perfection, etc.). The wide range of pre-exponential factor values observed can be qualitatively rationalized in terms of different amounts of diffusion (number of jumps) required to heal characteristic defects in particular microstructures. In non-graphitizing carbons, the graphitic (layer plane) structure is not sufficiently developed for graphitization to occur by this simple annealing process and conditions promoting a more complete structural reorganization are required. The influences of graphitization catalysts, hot-working and high pressures on graphitization can be qualitatively explained using this model in terms of their ability to promote structural reorganization, affect the self-diffusion rate, interact directly with structural defects, or influence the driving force for the transformation.

The Graphitization Process (continued)

Publications, Papers, etc.

D. B. Fischbach, "The Mechanism of Graphitization," paper presented at the joint NSF-JSPS Seminar on The New Materials Science of Carbon and Graphite in Tokyo, 9-12 Sept. 1970.

D. B. Fischbach, "The Graphitization Process," lecture presented at the 8th Japanese Summer Seminar on Carbon Materials, Wakayama, Japan, 3-5 Sept. 1970. Also presented at St. Mary's, Pa. 9 Nov. 1970 as part of Penn. State Univ. extension course on Unit Processes in the Carbon, Graphite and Powder Metallurgy Industries. To be published in Tanso (Japanese carbon journal).

D. B. Fischbach, "The Kinetics and Mechanism of Graphitization," in Chemistry and Physics of Carbon, P. L. Walker, Jr. edit., Dekker, N. Y. Vol. 7 (to be publ. Jan. 1971).

D. B. Fischbach, "On the Influence of Internal Stresses and Microstructure on Graphitization," paper in preparation.

The Structure and Graphitization Behavior of Pyrolytic Carbons Deposited in a Fluidized Bed

Faculty Supervisor: David B. Fischbach
Research Associate Professor
Ceramic Engineering

Graduate Assistant: Ronald L. Beatty, Ph.D. Candidate
Union Carbide Predoctoral Fellow

Objective: To investigate the influence of initial as-deposited microstructure on the graphitization behavior of pyrolytic carbons with a wide range of structures.

The deposition of pyrolytic carbon from hydrocarbon gases in fluidized beds has been extensively developed for coating microsphere nuclear fuel particles for high temperature gas-cooled reactors. This technique allows a wide range of deposition parameters (temperature, hydrocarbon gas type and concentration, substrate surface area, contact time, etc.) to be used, yielding a wide range of deposit microstructures. Both nearly isotropic and highly anisotropic carbons with a broad range of apparent crystallite size and layer perfection can be deposited. Low temperature isotropic deposits appear to have properties similar to those of glassy carbons, while high temperature columnar deposits resemble the substrate-nucleated pyrolytic carbons obtained by the hot-wall technique. The purity of the carbon is quite high, though low temperature deposits may contain significant amounts of hydrogen. Other studies have shown that the graphitization behavior of carbons depends sensitively on microstructure, but the influence of specific structural parameters is not yet clear. Furthermore, in conventional coke carbons, structural evolution in the pre-graphitization range below about 2000°C appears to differ fundamentally from that at higher temperatures. It is not clear at present whether this is due to impurities, excessive point defect concentrations, or other factors. Fluidized bed pyrolytic carbons appear to offer a family of materials very well suited to study of these problems. Furthermore, the graphitization kinetic behavior of these carbons has relevance to nuclear and other potential applications, but does not appear to have been extensively investigated to date.

Through the courtesy of members of the Oak Ridge National Laboratory staff, R. L. Beatty has used apparatus which he developed there to prepare a series of samples for study. Both carbon spheres (about 0.5 mm dia.), which formed the bed, and flat 0.010x0.25x0.25 in^3 plates of fine grained (POCO) graphite were used as substrates. Deposition temperatures of 1200-1900°C and a range of gas (propylene or methane) concentrations were used to prepare low temperature anisotropic (laminar) as well as isotropic deposits with a range of densities. Bed surface area and total gas flow rate were kept approximately constant for all deposition runs, and deposit thicknesses were about 150 microns. It is planned to characterize the structure and graphitization behavior by means of a variety of techniques such as dimensional change, metallography, x-ray diffraction, density and diamagnetic susceptibility as a function of heat treatment temperature and time. A set of density standards covering the range 1.3 - 2.3 g/cm^3 has been purchased, and a density gradient column has been designed. Several designs for small, inexpensive high temperature furnaces are being considered.

White Allotropic Graphite

Faculty Supervisor: David B. Fischbach
Research Associate Professor
Ceramic Engineering

Graduate Assistant: Robert M. Haugen, M. S. Candidate
Research Assistant

Objective: Attempt to verify the existence of a reported new allotrope of crystalline carbon and define conditions under which it forms.

It is generally accepted that hexagonal graphite is the only thermodynamically stable crystalline form of carbon at ambient pressures. Rhombohedral graphite, which can be characterized as an extensive stacking fault, is metastable and reverts to hexagonal graphite on annealing at high temperatures. Cubic diamond is stable only at high pressures and graphitizes at temperatures above about 1500°C at ambient pressure. It would be presumed that this is true of hexagonal diamond also. However, Whittaker and Kintner (Science 165 589, 1969) have reported that a white (or transparent) hexagonal allotrope of carbon formed on the layer-edge surfaces of pyrolytic carbon rods resistively heated to 2300-2700°C for 15-20 sec. in argon at 10^{-4} torr. If such an allotrope of carbon exists and is stable at ambient pressures and high temperatures, a major revision of the carbon phase diagram will be required. It would also open up exciting possibilities for new carbon materials.

The observations of Whittaker and Kintner have proved difficult to reproduce. Using experimental techniques similar to those they described, no deposits of white graphite have been produced to date. However, faint traces of a grayish deposit have been consistently observed on fracture surfaces of samples which failed at temperature. Attempts to determine the structure of these deposits by x-ray diffraction have so far failed. Further experiments are being planned on the hypothesis that the allotrope may deposit from ionized carbon vapor.

The Magnetic Behavior and Structure of Carbon Fibers

Faculty Supervisor: David B. Fischbach
Research Associate Professor
Ceramic Engineering

Graduate Assistant: C. Bruce Scott, M.S. Candidate
Research Assistant

Objective: To measure the diamagnetic susceptibility of carbon fibers and relate it to the structure to obtain further insight into the nature of these unique materials.

The diamagnetism of carbons and graphites is very anisotropic and highly structure-sensitive. The susceptibility measured parallel to the layers is small and results form the isotropic diamagnetism of the ion cores. The diamagnetism measured with the magnetic field normal to the layers is much larger (by about a factor of 70 in perfect single crystals) due to a Landau-Peierls type contribution from the free conduction electrons and holes in the layers. This component is very sensitive to the shape of the Brillouin zone and the position of the Fermi level and therefore quite structure-dependent. It increases with apparent layer-plane diameter, rapidly over the range 50-200 Å and more slowly above 200 Å. When the layer size is larger than about 150 Å, this anisotropic diamagnetism is also increased by layer stacking disorder. The total (tensor trace) susceptibility, which is the sum of the susceptibilities measured in three mutually perpendicular orientations of the sample, is independent of anisotropy and provides a measure of the crystalline perfection of the carbon. The dependence of the susceptibility on orientation, usually expressed by the anisotropy ratio (maximum over minimum value) is a measure of the orientation texture of the carbon. The unusual structure of high modulus carbon fibers, combining strong layer plane preferred orientation textures with appreciable crystallographic disorder, makes them particularly interesting materials for studies on strongly structure-sensitive properties such as magnetic susceptibility. This study was undertaken in the hope of advancing understanding of the magnetic behavior of carbons as well as gaining new insights into the structure of fibers, and perhaps developing alternatives to x-ray diffraction, metallographic and mechanical techniques for characterizing high performance carbon fibers.

The diamagnetic behavior of a broad selection of commerically available carbon fibers has been determined at room temperature by the Faraday technique using an electromagnet with specially shaped pole pieces and a recording semi-microbalance. The magnet was mounted on a turntable permitting rotation about the sample, suspended from the balance in a fixed orientation by a torsionally rigid holder, to facilitate anisotropy measurements. The apparatus has been calibrated against standard samples of platinum, copper, palladium and very high purity silver. Samples were made by tying fibers in parallel bundles about 1 - 2 mm diameter by 1 cm long weighing 10 - 20 mg. Susceptibilities were measured with the magnetic field parallel (χ_{axial}) and perpendicular (χ_{radial}) to the fiber axes. Then the total susceptibility $\chi_T = \chi_{ax} + 2\chi_{rad}$ and the anisotropy ratio is χ_{rad}/χ_{ax}. Precision and reproducibility of χ_T is very good, but scatter in the anisotropy ratio is fairly

The Magnetic Behavior and Structure of Carbon Fibers (continued)

large due to imperfect alignment of fibers within the bundles, and the small value of χ_{ax} (typically, for a high modulus fiber, $\chi_{ax} = 0.5$, $\chi_{rad} = 9$ giving $\chi_{\parallel} = 18.5$ in units of -10^{-6} emu/g and $\chi_{\parallel}/\chi_{\perp} = 18$). Measurements as a function of magnetic field strength have shown that the influence of ferromagnetic impurities is negligible. Measurements have been made on a series of rayon-precursor fibers with tensile modulus values ranging from 10 to 100 x 10^6 psi (Thornel fibers from Union Carbide Corp.), several grades of high strength and high modulus polyacrylonitrile-precursor fibers obtained from Hercules, Inc. and from Great Lakes Carbon Co., and low (10 x 10^6 psi) modulus fibers prepared from molten pitch by Kureha Chemical Co. Ltd. In general, it has been found that both the total susceptibility and the anisotropy ratio increases regularly as a function of Young's modulus (the Great Lakes fibers appear to be an exception). Furthermore, data for different types of fibers fall on different curves. These differences appear to result from different thermo-mechanical treatment histories as well as different precursors, and suggest the possibility of using magnetic measurements to characterize and identify carbon fiber types. A comparison of the magnetic behavior with x-ray diffraction structural parameters (data not yet complete) indicates a dependence of $\chi_{\perp}$ on the width of the layer-plane ribbons which make up the fibrile substructure of the fibers. Data collection for this project is now nearly completed.

Carbon as a Biomedical Material

Faculty Supervisor:	David B. Fischbach Research Associate Professor, Ceramic Engineering
Graduate Assistants:	J. Niles Research Associate, Biomedical Engineering
	M. Lapitsky, M.S. Candidate Research Assistant, Office of Engineering Research

Objective: The suitability of carbons and graphites as bone implant materials is being investigated with special attention to factors affecting bone ingrowth and adherence.

Among many factors affecting the use of synthetic materials in the human body, compatibility with the bio-environment is one of the most important for long-term applications, and one of the most difficult to satisfy. Because life is based on carbon chemistry and because pure carbons and graphites are chmically very inert, these materials appear to have great potential for biomedical applications. There has been considerable development of carbon materials for artificial heart valve and other circulatory system applications with very promising results. There has been somewhat less attention paid to carbon as an orthopedic material, though in previous work here a graphite sample performed very favorably in comparison with a variety of other ceramic materials.

A literature survey is being carried out and samples of porous carbons are being procured. It is planned to characterize the carbons by microscopy and porosimetry techniques before and after implantation in dogs leg bones. Studies are planned on bone ingrowth and the nature and strength of the carbon/bone interface.

Mössbauer Studies

Faculty Supervisor: Robert L. Ingalls
Associate Professor, Department of Physics

Graduate Assistants: Gerald A. Erickson, Ph. D. Candidate
Predoctoral Research Associate II

C.D. West, Ph. D. Candidate
Predoctoral Research Associate II

Objective: One object of this program is to apply the Mössbauer effect to study properties of various materials with emphasis on atomic force constants interatomic potentials, electron valence states and distributions.

Two programs involving the Mössbauer effect are currently in progress. The first, studies of the anharmonicity of the force constants of Fe^{57} in ThO_2 and UO_2 is nearing completion and will result in a Ph. D. degree for Mr. Erickson in the Spring of 1971. In many respects, the results in both materials are similar. In particular, the f-factors (recoiless fractions) and their temperature dependence are anamalously low, indicating large mean-square displacements because of the iron ion substituting for the larger host ions, Th^{++} or U^{++}. The anharmonic motion appears to be responsible for large thermal shifts and quadrupole splittings as well. At low temperatures, the results for UO_2 show a hyperfine pattern character of the magnetic ordering in this compound.

A second program Ph. D. thesis research of Mr. West, is concentrating on the surprisingly large anisotropy of the f-factor of Fe^{2+} in $FeSiF_6.6H_2O$. To date, the results contradict the results derived from x-ray diffraction and are not understood. A precision measurement of this anisotropy using the elliptical polarization of the Mössbauer γ-ray is in progress as a function of temperature for powder and single crystal samples. The study is also designed as a test for theoretical predictions on the dependence of the Mössbauer line shape on sample thickness when such anisotropy is present.

Publications

"Mössbauer Study of Low Temperature Anharmonicity in $ThO_2:Co^{57}$, by H. Shechter, J.G. Dash, G.A. Erickson and R. Ingalls. Physical Review 2B, 613 (1970).

Liquid Glass Phase Transition Study

Faculty Supervisor: Edward A. Stern
Professor, Department of Physics

Graduate Assistant: Dale Sayers, Ph. D. Candidate
Predoctoral Research Associate

Objective: A program of specific heat and extended x-ray absorption fine structure measurements of amorphous solids is also in progress. Its purpose is to examine the nature of the liquid to glassy state transition.

A study has recently been initiated (Mr. Sayers) to measure specific heats and extended x-ray absorption fine structure (EXAFS) for the liquid to glass transformation in an alloy sample of Au, Ge and Si. The most striking characteristic of this transformation is a rather sharp drop in the specific heat as the temperature is cooled below the transition temperature which suggests that the glassy state is inherently different from the liquid state. However, one possible explanation for this drop in specific heat has to do with the fact that because of the decrease in diffusion rate the sample may not be in thermal equilibrium under normal measurement times. In order to check this hypothesis, measurements of the specific heat are being made while changing the effective time of measurement by many orders of magnitude to see if the specific heat transformation temperature remains constant or varies. The latter possibility would indicate that what is being measured is a non-equilibrium property which would be extremely strong evidence that no transformation is occuring, but what is being seen is a change from equilibrium condiditions.

The EXAFS is also used to study the structure of amorphous solids. It has been shown that this fine structure is dependent on the short range order between the atom which absorbs the x-ray and the surrounding atoms. This technique is particularly suited for studying amorphous structures which have only short range order and can help determine if there is a structural change at the transformation.

Devitrification of Glass to Ceramic Seals

Faculty Supervisor:	James I. Mueller Professor, Ceramic Engineering
Graduate Assistant:	Alan Dall, B.S. Candidate Research Fellow (CMR-Tek)

Objective: The purpose of this research is to determine the mechanism of devitrification of glasses used for glass to ceramic seals.

The use of low-temperature, devitrifying glass to affect ceramic-ceramic or glass to ceramic seals is quite prevalent. The effectiveness of the seal is dependent upon the development of thin, but solid, glass-ceramic composite with appropriate strength and thermal expansion characteristics. Assurance of an adequate seal is dependent upon the proper thermal cycling of the glass to attain the appropriate degree of devitrification. An understanding of the effects of time, temperature and atmosphere is necessary in order to optimize the quality of the seal.

Several commercial seal materials are being studied. Differential thermal analysis (DTA) is being utilized to determine the temperatures at which melting and devitrification occur. High temperature x-ray diffraction (XRD) studies permit identification of the devitrification products and the kinetics of their formation, the effect of atmospheric pressure and composition can also be determined by these techniques.

Efforts to date have been limited to ambient atmospheric conditions. DTA studies have indicated the temperatures at which initial melting, devitrification, and secondary melting occur. High temperature XRD indicates that two devitrification phases occur, one of which resorbs or melts while the crystallinity and/or amount of the other increases over the high temperature range of the heating cycle. Definite identification of these phases has not been made to date.

It is planned to continue efforts towards identification of the two devitrification phases and to observe the effect of reducing atmospheres upon the reactions. The optimization of the thermal cycling should result when this knowledge of the overall reaction is attained.